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GRANT N0001400AF00002

PR Number 00PR01464-00

Technical Report No. 25

Percolation in S-SEBS and Fluorocarbon Proton Conducting Membranes

Prepared for publication in Macromolecules

by

C.A. Edmondson and J.J. Fontanella

Physics Department, U.S. Naval Academy, Annapolis, MD 21402-5026, USA

1 July 2000

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REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July 1, 2000	3. REPORT TYPE AND DATES COVERED Technical Report 6/1/99 to 5/31/00	
4. TITLE AND SUBTITLE Percolation in S-SEBS and Fluorocarbon Proton Conducting Membranes			5. FUNDING NUMBERS Grant Number: N0001400AF00002 PR Number: 00PR01464-00	
6. AUTHOR(S) C.A. Edmondson and J.J. Fontanella				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Naval Academy Physics Department Annapolis, MD 21402			8. PERFORMING ORGANIZATION REPORT NUMBER TR#25	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Physical S&T Div.- ONR 331 800 N. Quincy Street Arlington, VA 22217-5660			10. SPONSORING/MONITORING AGENCY REPORT NUMBER TR#25	
11. SUPPLEMENTARY NOTES Prepared for publication in Macromolecules				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS Electrical Conductivity, Complex Impedance, Percolation, Proton Conducting Membrane			15. NUMBER OF PAGES 16	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

Version: 7/19/00

Percolation in S-SEBS and Fluorocarbon Proton Conducting Membranes

C. A. Edmondson* and J. J. Fontanella

Physics Department, U.S. Naval Academy, Annapolis, MD 21402-5026, USA

Abstract—Electrical conductivity results at a variety of pressures, temperatures and water contents are evaluated for sulfonated styrene/ethylene-butylene/styrene (S-SEBS) triblock polymer, Nafion 117, and Dow 800 proton conducting membranes. In addition, room temperature and atmospheric pressure diffusion coefficients determined from conductivity and ^1H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies are considered. While the S-SEBS and fluorocarbons exhibit a percolation threshold at 10 and 4 wt-%, respectively, all materials exhibit this phenomenon at a volume water fraction of $C \approx 0.035$. Above the threshold the conductivity exhibits a power law behavior. When the volume of the hydrophobic portion of the membrane is subtracted the threshold occurs at the adjusted volume fraction of $C_A \approx 0.12$ which approaches that expected for continuum percolation.

INTRODUCTION

Sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer is employed by Dais-Analytic Corporation as a low cost proton conducting membrane for use in hydrogen fuel cells. S-SEBS is a relatively new material, with few papers describing the properties of this material.¹⁻³ S-SEBS is particularly interesting because of the structural differences between it and the widely studied Nafion and Dow materials.⁴⁻¹³ The important differences are both the composition of the backbone,

hydrocarbon vs. fluorocarbon, and nature of the sulfonate ion (connected via a benzene ring vs. fluorocarbon).

In a recent paper³ the authors presented a variety of experimental data for S-SEBS, Nafion 117 and Dow 800 including complex impedance/electrical conductivity and ¹H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies. Most of the data for both S-SEBS and the fluorocarbon-based material show the existence of a critical water content. This suggests the possibility that a percolation threshold exists. In fact, percolation theory has been applied to Nafion, albeit with limited success.^{14,15} In the present paper a detailed discussion of the application of percolation theory to S-SEBS and fluorocarbon based proton conductors is given. It is shown that when the water is properly accounted for, percolation theory results in an excellent representation of the data.

DISCUSSION

Figure 1 is a plot of electrical conductivity vs. water content from reference 3 for three proton conducting membranes. The general behavior is the same for each of the polymers and may be considered in terms of two regions. In the first region the conductivity is high for high water content and decreases approximately in proportion to the water volume fraction until a critical value is reached. Below the threshold, in the second region, the conductivity is low. Of particular interest is that the threshold differs significantly between S-SEBS (approximately 10 wt%) and the two fluorocarbon polymers (approximately 4 wt%). The existence of a threshold suggests the applicability of percolation theory.

Percolation theory is usually discussed in terms of the volume fraction of water, C , which is given by:

$$C = \frac{V_{\text{water}}}{V_{\text{total}}} = \frac{V_{\text{water}}}{V_{\text{water}} + V_d} \quad (1)$$

where V_{water} is the volume of the water and V_d is the volume of the dry polymer.¹⁵

Figure 2 is a plot of the electrical conductivity vs. C for the three proton-conducting polymers. While the general behavior is the same as in figure 1, a significant difference is observed in that the threshold is about the same, ≈ 0.05 , for all three polymers. However, each of the materials exhibits a slightly different dependence on C above the critical concentration.

The existence of this threshold can be further demonstrated by considering the behavior of the diffusion coefficient as a function of water content. In figure 7 of reference 3, D_σ and D are plotted vs. water uptake in S-SEBS and Nafion 117 in wt-%. D_σ is the diffusion coefficient determined from conductivity using the Nernst-Einstein relation while D was measured using ^1H pulse gradient spin-echo nuclear magnetic resonance.³ For S-SEBS both techniques yielded a threshold value of approximately 10 wt-% water and for Nafion 117 the value was approximately 4 wt%. Figure 3 is same data plotted vs. the volume fraction of water, C . Both D_σ and D for both S-SEBS and Nafion 117 show a threshold at $C \approx 0.05$.

Figure 4 is a log-log plot of electrical conductivity vs. water content for the three proton conducting membranes. Again the data are taken from reference 3. The vertical dashed line represents the logarithm of the approximate threshold ($C=0.05$). To the right of this line the approximately linear behavior at high water content suggests that a power law, and hence percolation, should be considered when attempting to explain the results.

The reason, of course, is that in percolation theory the conductivity is expected to obey the following law:¹⁶

$$\sigma = \sigma_o (C - C_o)^r \quad (2)$$

C_0 is the critical volume fraction required for ions to percolate and n is referred to as a critical exponent which controls the scaling behavior.

To test the theory, C_0 initially was arbitrarily chosen and $\log \sigma$ vs. $\log(C-C_0)$ was best fit to the data for $C > C_0$. This procedure was repeated for various values of C_0 until a maximum in the linear correlation coefficient was achieved. The results of the linear regression analysis are listed in Table 1 and the data and best-fit curve for S-SEBS are shown in figure 5.

The three polymers yield C_0 values that range from 0.03 to 0.04 and n values that range from 1.3 to 1.5. In lattice percolation theory, where the conducting elements occupy a well defined periodic lattice, the expected value for n is well defined and is a function of system dimensionality. The observed values of n fall in the expected range (1.5 ± 0.2) for a theoretical 3D lattice.^{15,17} In continuum percolation theory, where no periodic lattice exists, the value for n is not as well defined but seem to follow those of conventional lattice percolation.¹⁶ However, in all theories, C_0 is well defined and the observed values ($C_0 \approx 0.035$) are much lower than the values that are typical of percolation. For example, for continuum percolation on a random close pack structure a value of $C_0 = 0.16$ is expected.¹⁶

There are several possible causes of the anomalously low values of C_0 . Hsu et al. have suggested that if the water is spread into a more extended, uniform network then a lower critical concentration would be expected.¹⁵ However, as is discussed by Pourcelly and Gavach,¹⁴ a number of experimental results for Nafion suggest a non-uniform distribution of water. Even though there is doubt concerning the original model of spherical clusters of water in Nafion,^{19,20} because of the distribution and effect of the sulfonate ions, it is unlikely that sufficient uniformity can be achieved to explain the results.

Another possible cause of the anomalously low values of C_o would be a very large coordination number. This decreases the percolation threshold by increasing the number of conduction paths. However, x-ray evidence suggests that the coordination number for water is approximately 4.4 at room temperature, a vestige of the tetrahedral structure of ice.²¹ Consequently, it is unlikely that a large coordination number exists in these materials.

A more reasonable explanation can be given by reconsidering the way in which the volume fraction is calculated. In percolation theory, all quantities refer to the conducting phase. However, in the case of the proton-conducting membranes a fraction of the material is inert. For example, the hydrophobic regions of Nafion have nothing to do with the conduction process i.e. when water is added to the polymer, the polymer is not replaced. Consequently, a more appropriate approach is to only consider the volume that is available to the water. In this case the volume fraction is given by:

$$C_A = \frac{V_{water}}{V_{water} + V_d - V_p} \quad (3)$$

where V_p is the volume occupied by the polymer that is not available to water. It is assumed that the sulfonate group is not included in V_p .

An estimate of V_p was made as follows. For Nafion 117 and Dow 800, the density of the polymer was taken to be 2.3 g/cm³, which is the value for poly(tetrafluoroethylene).²² For S-SEBS, since the density of each of the constituents is within approximately 7% of that for water, a value of 1.0 g/cm³ was used. Using these approximations, the revised volume fraction available to water, C_A , was calculated. Using the previous fitting technique, the parameters in the following equation:

$$\sigma = \sigma_{Ao} (C_A - C_{Ao})^{n_A} \quad (4)$$

were evaluated and the results are listed in Table 1. The data and best fit curve for S-SEBS are shown in figure 6. The parameter of interest, C_{Ao} , is 0.105 for S-SEBS, 0.11 for Nafion 117, and 0.14 for Dow 800. These values approach the expected volume fraction for continuum percolation. The critical exponent for the available volume, n_A , ranges from approximately 1 to 2.1. While these values cover a broader range than the total volume critical exponent, n , they are not unreasonable for continuum percolation.

It is important to note that present model neglects the swelling of the polymer which would tend to increase the available volume. It will be of interest to investigate the effect of swelling on the percolation model.

CONCLUSION

In summary, proton transport in these membranes depends on the volume water fraction and exhibits a percolation threshold. Above the threshold the conductivity vs. volume water fraction follows a power law. When the volume available to the water is properly accounted for percolation theory may be used to describe the observed conductivity.

ACKNOWLEDGEMENTS

The authors would like to thank M.F. Shlesinger of ONR and J.T. Bendler of the South Dakota School of Mines and Technology for useful discussions concerning percolation. This work is supported in part by the US Office of Naval Research.

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Table 1. Percolation Fit Parameters.

	C_0	n	σ_0 (S/cm)	C_{A0}	n_A	σ_{A0} (S/cm)
S-SEBS	0.04	1.47	0.685	0.105	0.96	0.207
Nafion 117	0.03	1.38	0.272	0.11	2.1	0.115
Dow 800	0.035	1.31	0.259	0.14	1.75	0.125

FIGURE CAPTIONS

Figure 1. Conductivity vs. weight percent water for Nafion 117, S-SEBS and Dow 800.

Figure 2. Conductivity vs. volume fraction water for Nafion 117, S-SEBS and Dow 800.

Figure 3. The Diffusion Coefficients D and D_g vs. volume fraction water for S-SEBS and Nafion 117.

Figure 4. Log_{10} - Log_{10} plot of the conductivity vs. volume fraction water for Nafion 117, S-SEBS and Dow 800. The vertical dashed line represents the approximate threshold of $C=0.05$.

Figure 5. Best fit results for conductivity vs. volume fraction water minus the percolation threshold for S-SEBS.

Figure 6. Best fit results for conductivity vs. volume fraction available to water minus the percolation threshold for S-SEBS.

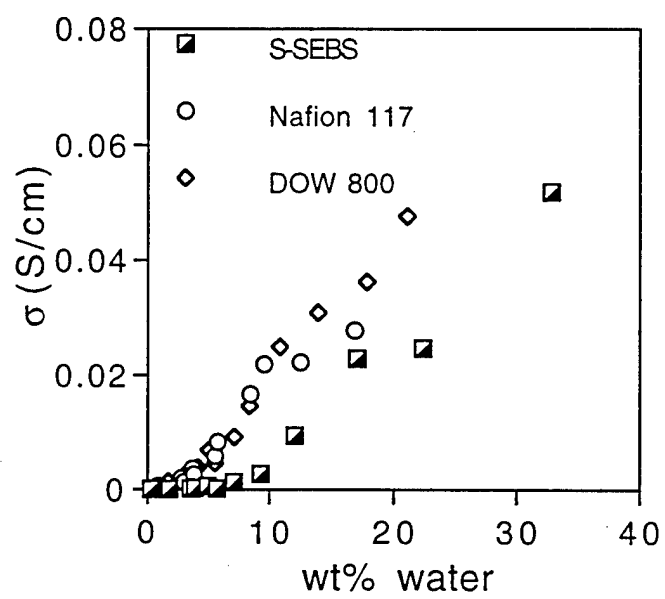


Fig. 1

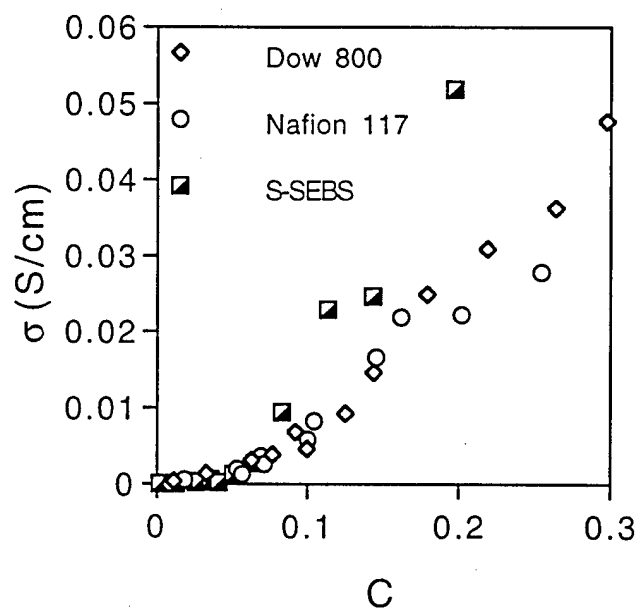


Fig. 2

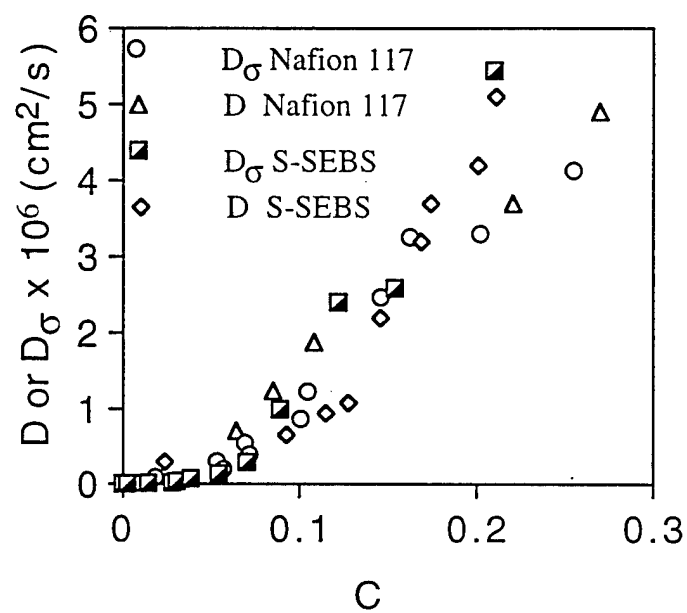


Fig. 3

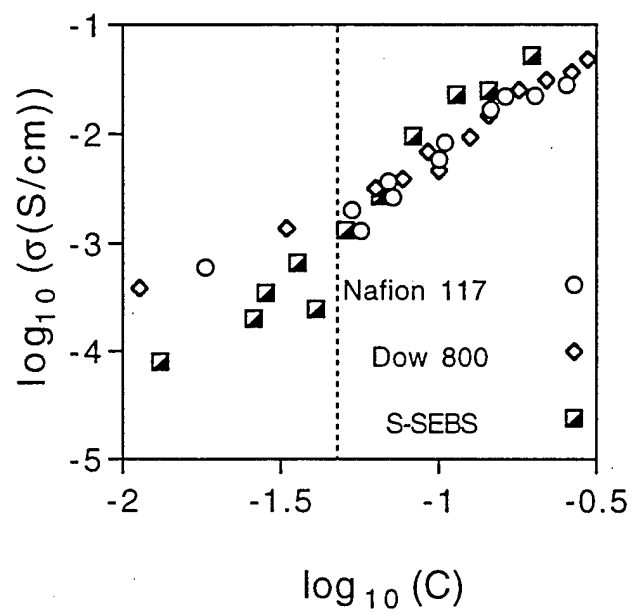


Fig. 4

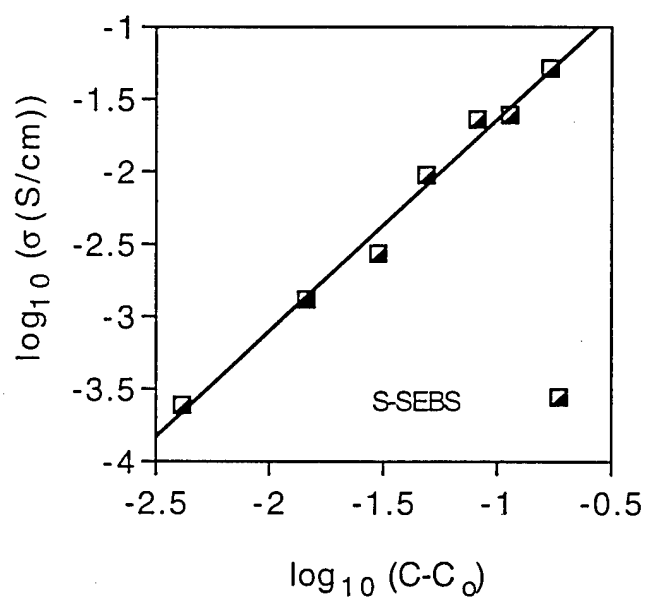


Fig. 5

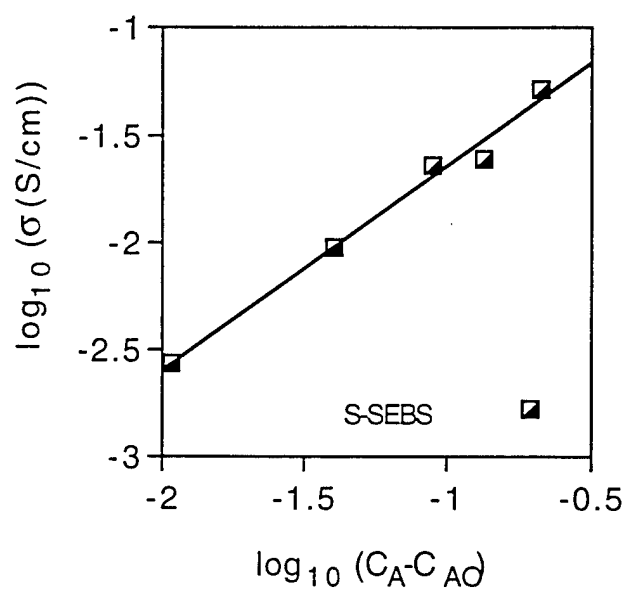


Fig. 6